WADC TECHNICAL NOTE 59-258

AN EXPERIMENTAL INVESTIGATION ON THE CHEMISTRY AND INTERCONVERSION OF BORON HYDRIDES

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WRIGHT AIR DEVELOPMENT CENTER
AIR RESEARCH AND DEVELOPMENT COMMAND
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FOREWORD

This report is a summary of research carried out under Project 3048, Task 70321, "An Experimental Investigation of the Chemistry and Interconversion of Boron Hydrides," under Contract AF33(616)-5827 during the period July 1, 1958 to June 30, 1959.

Experimental studies reported herein were carried out largely by Mr. Gerald Brennan, Mr. Rudolph Buttlar, Mr. Richard Enrione, Mr. Louis Ross and Mr. Frederick Tebbe. Mr. Gerd Dahl, Miss Josephine Lippard and Mr. Martin Thompson were of considerable assistance in the early portion of the contract and their aid in establishing the laboratory facilities. Miss Elizabeth Greene was of invaluable assistance in the preparation of the manuscript.

This contract was administered by the Chemistry Research Branch, Aeronautical Research Laboratory with Dr. William L. Ruigh as task scientist for WADC.

ABSTRACT

A novel method for preparing diborane by radical catalyzed reaction of trichloroborane and monosilane is described.

Experimental studies of various steps in the thermal conversion of diborane to pentaborane-11 are described. These include a study of the isotope effect on diborane pyrolysis, reaction of a possible triborane with diborane and isolation of tetraborane-8 carbonyl as an intermediate in tetraborane pyrolysis.

Our presently preferred mechanism for diborane pyrolysis is:

$$B_2H_6 = 2\ BH_3$$

$$BH_3 + B_2H_6 = B_3H_9$$

$$B_3H_9 \rightarrow B_3H_7 + H_2$$

$$B_3H_7 + B_2H_6 \rightarrow B_4H_{10} + BH_3$$

$$B_4H_{10} \rightarrow B_4H_8 + H_2$$

$$B_4H_8 + B_2H_3 = B_5H_{11} + H_2$$

Physical properties of tetraborane-8 carbonyl including vapor pressures, infrared spectrum, NMR spectrum and mass spectrum are reported.

Reaction of bridge labelled decaborane with acetonitrile released hydrogen of deuterium content corresponding closely to release of one bridge and one non-bridge (probably 5,7,8,10) proton.

Reaction of bridge labelled decaborane with CH_3MgI produced about 25% CH_3D. Attack at the top of the molecule is indicated.

A new amine derivative of a borane has been obtained by treatment of $(CH_3)_3NB_3H_7$ with hydrogen chloride and diborane. On the basis of incomplete data it has been assigned the formula $(CH_3)_3NB_4H_9Cl$. A second new, but as yet unidentified substance is formed when diborane is omitted in the above treatment.

Several attempts to isolate a new solid borane are described.

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SECTION I*

THE PREPARATION OF DIBORANE

The preparation of diborane has hitherto been carried out by one of three reactions:

a) By hydrolysis of suitable metallic borides,[1]

b) Reaction of a boron halide with hydrogen under suitable conditions (such as in an electric arc)[2]

c) The reaction of a boron halide or similar compound with a non-volatile metal hydride or complex hydride.[3]

Preparation of diborane by a route not involving a metal hydride but of more convenience than methods a or b seemed to interest.

Calculations based on bond energies indicate that the formation of diborane by reaction of silane with trichloroborane should be slightly exothermic. A radical chain process seemed to offer a promising mechanism for achieving hydride transfer. It was subsequently found that mixtures of SiH_4 and BCl_3 do react in the presence of methyl radicals to produce diborane in good yield. Using the photochemical decomposition of azomethane as a source of methyl radicals, the reaction products were found to be diborane, methane and both mono- and dichlorosilane.[4] In addition, a considerable amount of non-volatile substance was produced in the reaction. In the initial experiment, 0.19 mmoles of azomethane was decomposed in a 50 ml. Pyrex bulb by ultraviolet irradiation for a period of 45 minutes in the presence of 4.57 mmoles

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*Manuscript released by Author, July, 1959.

of SiH_4 and 1.52 mmoles of BCl_3. A 67% yield of diborane (0.51 mmoles) was isolated by fractionation through a -135° trap; none of the silane was recovered as such but about 68% was isolated as chlorinated derivatives and the remainder was contained in the non-volatile product. No unreacted BCl_3 was recovered; therefore, some boron also appears to have been contained in the non-volatile fraction. Two additional mixtures (with silane in two-fold excess) were allowed to react for irradiation periods of 5 minutes and 15 minutes. In these cases, the excess silane remained in the reaction products and was difficult or impossible to separate from the diborane by fractional condensation in a vacuum system. Thus, the yield of diborane was not calculated, although the reaction did appear to be complete after these shorter periods of time. A method has been devised by which the relative amounts of SiH_4 and B_2H_6 can be determined in mixtures of the two by means of the mass spectrometer, but further reactions of this type have not yet been run. The reactions thus far have been carried out at room temperature and in all cases some non-volatile material was produced. It has been observed in recent experiments that a nonvolatile product is formed directly from azomethane and boron trichloride. Presumably catalysis occurs by decomposition of only a fraction of the azomethane added. Clearly some methyl radicals are produced since methane is a major product. Further studies of this aspect of the reaction will be required.

Since methane was among the products and no methyl chloride was observed, it appears that the first step in the reaction involves the attack of the methyl radical on SiH_4 rather than on BCl_3. The probability of such attack was further substantiated by noting only partial recovery of silane when mixtures of silane and azomethane were irradiated with ultraviolet

light. In one trial, 83% of the silane was recovered after a 25 minute irradiation and in a second trial, 67% of the silane was recovered after a 60 minute irradiation. No attempt has yet been made to identify products of this reaction.

Consideration of the above facts suggests a possible chain mechanism for the hydride transfer:

(1) $CH_3N{=}NCH_3 \xrightarrow{h\nu} 2\cdot CH_3 + N_2$

(2) $SiH_4 + \cdot CH_3 \rightarrow CH_3 + \cdot SiH_3$

(3) $BCl_3 + \cdot SiH_3 \rightarrow SiH_3Cl + \cdot BCl_2$

(4) $SiH_4 + \cdot BCl_2 \rightarrow HBCl_2 + \cdot SiH_3$

(5) $6HBCl_2 \rightarrow B_2H_6 + 4\,BCl_3$

The existence and disproportionation of $HBCl_2$ has been previously observed. Alternatively, further attack on the $HBCl_2$ species may occur. Either pathway leads to the same observed product and experimental choice between the two would be difficult. To obtain more information on the mechanism of the reaction the reaction of mixtures of BCl_3 and azomethane under ultraviolet radiation will be studied.

The clear, viscous, non-volatile reaction product was soluble in carbon disulfide; the infrared spectrum showed adsorption at 3.9 microns indicating the presence of boron-hydrogen bonds, as well as strong adsorption indicating silicon-hydrogen bonds. Removal of the CS_2 left a material which dissolved in dilute sodium hydroxide to form a solution which reduced silver nitrate. Prolonged exposure of the original material to air converted it to a water-soluble, white solid.

A preliminary experiment indicated that iodine is also capable of initiating the reaction of SiH_4 with BCl_3. Experiments using iodine as the initiator are difficult owing to the mercury normally present in the system. Diborane has not yet been isolated from this reaction mixture but further experiments are planned.

During the coming year other radical initiators will be investigated as will the possibility of using substituted silanes and other boron halides.

SECTION II

THE CONVERSION OF DIBORANE TO PENTABORANE-11

Introduction

Methods for the preparation of the boron hydrides have been strictly limited in their generality. In his classic and pioneering studies of the boranes, Stock found that most of these unique compounds could be prepared by hydrolysis of magnesium boride.[1] He also found at an early stage in his investigations that the primary product of the hydrolysis, B_4H_{10}, could be readily converted to other boranes by heating at 100° for short periods and that other boranes could be interconverted in similar manner. This observation became of considerably greater practical importance when the studies of Schlesinger and coworkers resulted in much simpler methods for the preparation of diborane wherein other boranes were not simultaneously produced.[2,3] Preparation of higher boranes in the last twenty years has consequently been almost universally carried out by pyrolysis of diborane under a variety of conditions and is of considerable technological importance. In addition, the fascinating structures of the boranes make the interconversion problem one of tantalizing scientific interest.

Recently there have been reports of chemically produced interconversions of boranes (see for example recent papers by Burg and coworkers[5,6]). We shall confine our attention here, however, strictly to the thermal process occurring at about 100°C.

Several groups have examined the kinetics of pyrolysis of diborane.[7,8] The most complete data available to us is that of Bragg, McCarty and Norton who followed both the rate of pressure rise and the rate of hydrogen formation and in addition carried out a more complete analysis of reaction products using a mass spectrometer. All data available seem strongly to support the fact that diborane decomposes by a 3/2 order reaction. The generally accepted interpretation of this observation is that diborane is in facile equilibrium with borane groups and the rate controlling

step of the reaction involves a molecule containing three boron atoms. No convincing data are available to permit a more precise statement of the nature of the rate controlling step. It seems worthwhile to present certain speculations about the reaction intermediates.

The precise nature of the chemical reactions occurring beyond this point in the decomposition of diborane are primarily matters of speculation. It has been a primary purpose of this project to gather additional information to attempt to elucidate the reactions taking place.

Conversion of Diborane to a Triborane

The kinetic data quoted above clearly indicate the intermediate existence of a triborane as a reactive intermediate in the pyrolysis of diborane. Three simple postulated mechanisms for this reaction may be examined in detail (it is by no means intended to imply that others cannot be conceived). If only reactions involving species with even numbers of electrons are considered, three reactions seem possible.

(6) $BH_3 + B_2H_6 \rightarrow B_3H_7 + H_2$

(7) $BH_3 + B_2H_6 = B_3H_9$

(8) $B_3H_9 = B_3H_7 + H_2$

Reaction (6) may be considered to be a concerted reaction in which hydrogen is eliminated as BH_3 enters the molecule. In the plot of energy vs. reaction coordinate shown in Figure 1 this corresponds to an energy maximum for the composition B_3H_9. Alternatively, reactions 7 and 8 might together more properly describe the reaction sequence. Curves of energy vs. reaction coordinate will in this case have the form shown in Figure 2 with the highly reactive molecule B_3H_9 present in an energy minimum either following or preceding the highest hill in the potential energy curve depending on whether reaction 7 or 8 is rate limiting.

A number of observations (none of a wholly conclusive nature) make it desirable at the present time to include B_3H_9 as at least a metastable intermediate,

Figure 1

Energy vs. Reaction Coordinate for the Case

Wherein No Intermediate B_3H_9 is formed

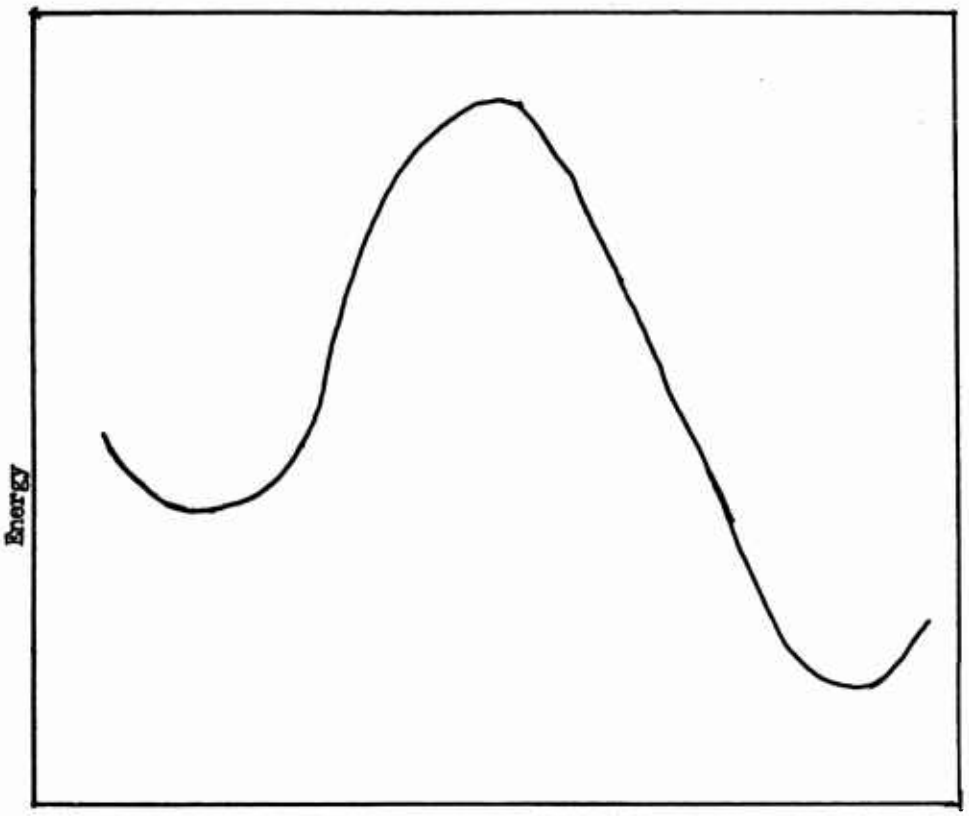
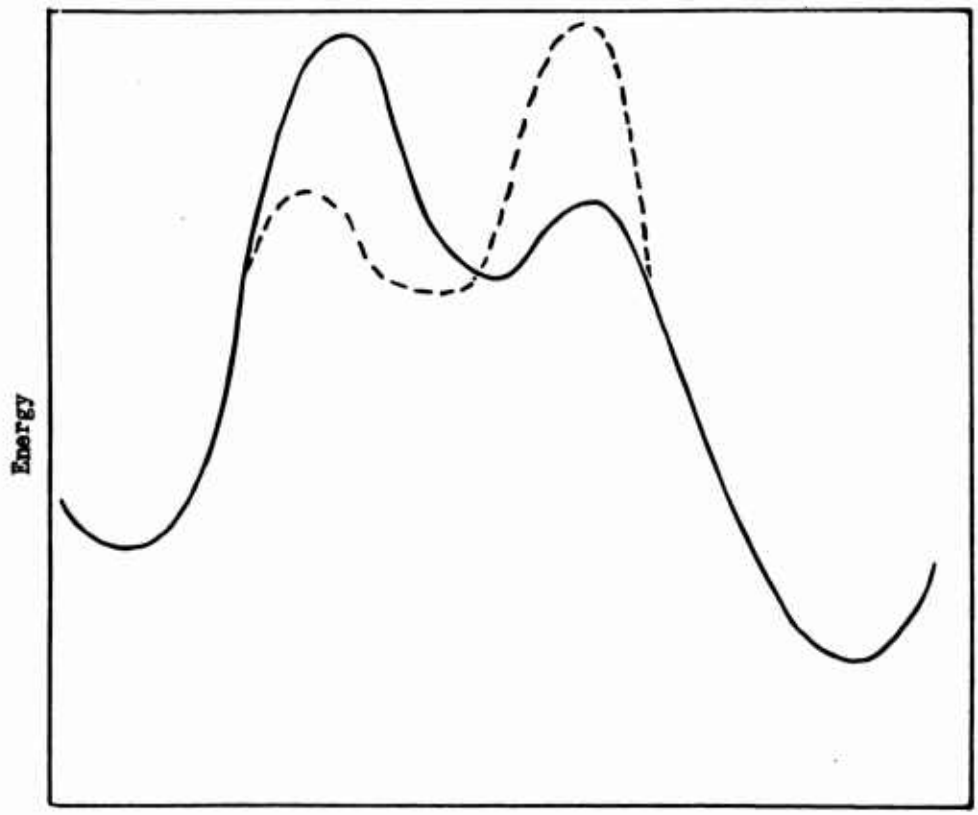


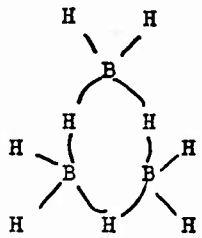
Figure 2

Energy vs Reaction Coordinate for the Cases

Wherein B_3H_9 is an Intermediate



thus eliminating reaction 6 as the reaction pathway. A satisfactory structure for the B_3H_9 molecule can be written using the semitopological appraoch of Dickerson and Lipscomb.[9] According to this approach structures of the 3003 type* only are possible and the unique structure derived for this molecule is



This molecule may be considered in principle to be the parent acid which gives rise to salts containing $B_3H_5^-$ ion.[10] Furthermore, several reactions of diborane have been reported wherein hydrogen was not lost but 3/2 order kinetics were followed. A typical example of such a reaction is the exchange which occurs between B_2H_6 and B_2D_6. It is tempting to invoke the symmetrical B_3H_9 molecule as an intermediate in these reactions and to also retain it as an intermediate in diborane decomposition.

Limiting consideration in light of the above comments to reactions 7 and 8, no prior study has given information enabling a decision to be made as to which is the rate limiting step. However, if reaction 8 is rate limiting, a substantial isotope effect on the rate of decomposition should be observed by replacing hydrogen with deuterium in the molecule, whereas no such substantial effect should be observed if reaction 7 is rate limiting. Preliminary experiments have now been carried out to compare the rate of decomposition of diborane with that of deuterodiborane.

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*In this presentation of structural information the first figure gives the number of hydrogen bridges, the second the number of three center bonds containing three boron atoms, the third figure gives the number of direct, single B-B bonds and the last may be regarded as being the number of BH_2 groups in the molecule.

Experimental.- The apparatus used in these investigations consisted of a 500 ml. reaction bulb immersed at all times in an oil bath thermostated at 78.8°C and connected by a capillary tube to a stopcock above the oil level. The reaction vessel was connected to two U-tubes packed with Pyrex glass wool and then via a second stopcock to the vacuum system containing a Toepler pump. With the reaction bulb at operating temperature and thoroughly evacuated, a measured quantity of diborane or deuterodiborane was expanded into the two U-tubes maintained at room temperature. When all of the diborane had evaporated the stopcock leading to the reaction bulb was opened for five seconds, closed and the residual diborane contained in the U-tubes measured. By this technique approximately 60 percent of the initial diborane entered the reaction bulb and would be expected to reach thermal equilibrium with the heated walls within a relatively short time. After a desired time interval the reaction was terminated by opening the stopcock and allowing the gases to expand through the two U-tubes (now cooled with liquid nitrogen) into a total volume of 3660 ml. The total pressure dropped at once to less than three tenths of a millimeter. At this pressure the rate of decomposition of diborane was considered to be negligible during the time necessary to remove the hydrogen formed by the earlier decomposition.

Results of this investigation are as yet only highly preliminary but it may be seen by examination of Table 1 that agreement between rate constants determined here and those determined by previous workers is moderately good although improvement may be expected as the technique is perfected. Preliminary value of the ratio of the rate constant for B_2H_6 to that for B_2D_6 is about 4.5. The overall rate constant determined involves both the rate constant for the reaction and the square root of the equilibrium constant for the dissociation of diborane to two boranes. Approximate calculations for the dissociation lead to an equilibrium constant for the deuterium case only 0.25 as large as for the protium case. The ratio of rate constants corrected for the square root of this factor is thus about 2.3.

Table 1

Relative Rates of Thermal Decomposition of Diborane and Deuterodiborane

Sample No.	C_o Initial Concentration Diborane Moles/Liter X 10^3	C_H Moles/Liter H_2 Evolved X 10^5	Time Hours	$k = \frac{C_H}{C_o^{1.5} t}$ (Liter/Mole)$^{0.5}$/Hr.
		Pyrolysis of B_2D_6		
I	14.12	5.48	.350	.0934*
II	14.16	3.10	.500	.0367
III	14.20	4.30	.666	.0381
IV	13.86	7.48	1.00	.0458
		Pyrolysis of B_2H_6		
I	13.82	11.44	.333	.211
II	14.46	8.05	.250	.185
III	14.22	10.06	.292	.202
IV	14.40	5.24	.1665	.182
V	20.64	9.06	.1665	.183

*The high value obtained in the first experiment was probably due to some residual moisture on the bulb walls.

Approximations to the maximum expected isotope effect (if the boron-hydrogen bond is completely broken in the transition state) have been made using the bridge and terminal stretching frequencies of diborane. The expected value is about 3.7 per terminal boron hydrogen bond broken or 2.8 for rupture of a bridge bond. Thus it appears that the isotope effect is too large to be explained by the assumption that formation of B_3H_9 (reaction 7) is rate limiting and is in approximate agreement with the effect expected if reaction 8 is rate limiting. More detailed studies of this system will be carried out during the coming year including the studies of the temperature effect on the isotope effect.

Unsuccessful Attempts to Prepare $B_3H_8^-$ Salts from Diborane

Following considerations presented above for the possible importance of B_3H_9 as an intermediate in the decomposition of diborane, some effort was devoted to the possibility of isolating $B_3H_8^-$ salts by abstraction of a proton from a B_3H_9 intermediate. It was clearly necessary to utilize a Lewis base incapable of direct attack on a boron acid but capable of interaction with a proton. Such requirement puts stringent limitations upon the systems which can be used. Two organic amines, N,N'-2,6-tetramethyl aniline[11] and 2,6-di-t-butylpyridine[12] have been prepared which might be suitable. The aniline derivative was utilized for the experiments listed in Table 2. In most cases traces of a non-volatile white solid were produced but in no cases were the amounts of materials produced sufficient to permit positive identification of the product. Reactions were carried out at pressures as high as 650 PSIG to enhance the concentration of B_3H_9 intermediate and at room temperature to limit the decomposition of diborane.

Table 2

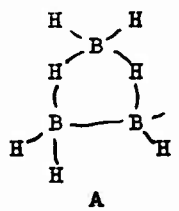
Reaction of Diborane with N,N',2,6-Tetramethyl Aniline

Run	PSIG Initial	°C Temp.	Time	mmoles base	mmoles B_2H_6 orig.	Solvent	mmoles B_2H_6 rec.	mmoles H_2 rec.	Remarks
1	15	50 80	15 min 15 min	3	.525	None	.126	Trace	No solid formed
2	15	RT	2 hr	3	.808	None	.726	.19	No solid formed
3	75	RT	2 hr	6	2.25	None	2.25	.03	Trace white solid
4	150	RT	24 hr	6	4.10	None	4.03	.024	Trace white solid
5		RT	15 hr	6	2.25	1 ml ET_2O	2.15	.034	Trace white solid, RX vessel 10-15 ml
6		RT	15 hr	6	2.15	1 ml THF	2.10	.035	Trace white solid, RX vessel 10-15 ml
7		RT	10 days	6	2.22	1 ml n-Hexane	2.15	.112	Trace white solid, RX vessel 10-15 ml
8		RT	11 days	18	11.34	THF	5.60	3.13	Small amount nonvolatile liquid RX vessel 50 ml vol.
9	250	RT	2 days	100	48.7	None	46.0	1.50	Trace white solid
10	360	RT	5 days	100	71.0	None	67.8	5.83	Small amount white solid 1.76 mmoles B_4H_{10} recovered
11	460	RT	6 days	100	120.85	None		12.02	Trace white solid
12	650	RT	2 days	100	240	None	223	16.62	Small amount white solid 6.7 mmoles B_4H_{10} 1.7 mmoles B_5H_9 recovered
13	470	RT for 4 days 50 0 for 2 days			244	20.4 mmoles ET_2O	222	20.2	B_4H_5 not rec. B_6H_{10}-small amt. isolated. Very small amt. white solid
14	400	0	2 days	None	254	None	254	.217	---
15	635	RT	2 days	None	254	None	252	2.16	---
16	550	RT	2 days	50	252	None	245	7.73	Small amt. white solid

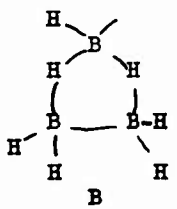
Reaction of a Triborane with Diborane

Arguments presented in the sections above lead to the conclusion that a triborane containing seven hydrogen atoms is formed in the rate limiting step of the decomposition of diborane. Application of the topological theory of Lipscomb allows derivation of two suitable descriptions of the B_3H_7 molecule. Although either a 3011 or a 2102 arrangement of bonds satisfy the equations of balance for this system, no satisfactory structure for the molecule can be written based on an icosahedral fragment utilizing the additional assumptions of the topological theory. The existence of both amine and ether adducts of the B_3H_7 molecule suggests that a more satisfactory treatment of its structure could be based on the assumption that one orbital is unused for bonding within the compound (that is, that the molecule is a Lewis acid in the same sense as the borane molecule). Derivation of suitable equations to describe the topological structure of any boron hydride with an unfilled orbital may be readily carried out.

Let s stand for the number of B-H-B bonds in the molecule, t for the number of three center boron bonds, y for the number of direct boron-boron bonds and x for the number of BH bonds in excess of one per boron. As in the case of boranes themselves, of the general formula B_pH_{p+q}, hydrogen balance for the system requires that $s + x = q$. Similarly electron balance in the molecule requires that $2t + 2y = 2p - q$. However, derivation of an orbital balance equation leads to the alteration $s + t = p - 1$. Application of these equations to the B_3H_7 molecule lead to 1103 and 2012 types. No satisfactory structure can be derived for the 1103 type since all such structures necessarily require simultaneous bonding of two borons by a hydrogen bridge bond and by a three center bond. However, two possible structures of the 2012 type can be derived as shown below.



A



B

Structure A appears to be preferred by Nature, at least in the case of the stable trimethyl amine addition product.[13] It may be observed that the recent work of Rice[14] indicates that the borane molecule will be expected to have pyramidal structure with some electron density in a fourth orbital occupying the remaining tetrahedral position. Similar-stabilization of the vacant orbital in the B_3H_7 molecule might occur.

The fate of the B_3H_7 molecule in the thermal decomposition of diborane is a matter of considerable interest and speculation. Some authors have preferred to write tetraborane-10 as the product formed from the triborane whereas others have preferred pentaborane-11. It appeared of interest to attempt experiments to provide supplementary information on this point.

It has previously been shown by Schlessinger and Brown[15] that treatment of solid sodium borohydride with gaseous hydrogen chloride produces sodium chloride, hydrogen, and diborane. No direct studies of the mechanism of this reaction have been carried out but two possible reaction patterns can readily be visualized. Direct displacement of the hypothetical weak acid HBH_4 from the borohydride might occur with subsequent decomposition to hydrogen and borane, and dimerization of borane groups. (It should be observed that only eight electrons are present although five atoms are bonded to boron.) Alternatively, the direct acid attack might take place at the borohydride group with the evolution of hydrogen and formation of borane. As in the previous case of the B_3H_9 intermediate the distinction is basically one of the possible metastable existence of the intermediate molecule. The fact that HD can be prepared in high purity from the reaction of sodium borohydride with deuterosulfuric acid suggests that in this case no stable intermediate exists and the second pathway is to be preferred. (It of course shows only that no randomization of protons occurs within any such intermediate molecule.)

If sodium borohydride in the above reaction is replaced by sodium triborohydride (NaB_3H_8) two possible reactions paths again may be considered. By analogy with the sodium borohydride reaction one might expect direct loss of hydrogen as a result of

attack of the acid on the anion leading to the formation of B_3H_7. Alternatively, the intermediate molecule B_3H_9 might be generated. Late in the course of this investigation personal communication from Professor Parry of the University of Michigan indicated the likelihood that at least a substantial fraction of the reaction of an acid with NaB_3H_8 involves loss as hydrogen of only about 1/9 of the acid protons fitting well with the scheme in which B_3H_8 is produced as an intermediate. The B_3H_9 molecule generated in this fashion may be expected to undergo simultaneous decomposition by two pathways, one leading to the formation of diborane and the other to the formation of B_3H_7 and hydrogen. It should be noted that B_3H_9 concentrations may be expected to be substantially higher in the present case than in the case where this molecule is generated by thermal decomposition of diborane and consequently no simple predictions can be made as to the ratio of rate constants for the two paths.

The possibility of generating B_3H_7 in the presence of diborane under conditions such that the initial product of the subsequent reaction would be stable should provide interesting information concerning the pathway followed in the thermal decomposition of diborane where subsequent reaction of the initial reaction product may readily occur.

Experimental.- All experimental investigations of the reaction of a mixture of hydrogen chloride and diborane with solid sodium triborohydride were carried out in a conventional vacuum system.[16] Infrared spectra were obtained with a Perkin-Elmer Infracord Spectrophotometer and mass spectra were obtained with a Consolidated Engineering Corporation model 21-620 mass spectrometer. Powder patterns were obtained with a Norelco geiger counter scanning instrument.

Because of difficulties to be mentioned below in the reaction of NaB_3H_8 some experiments using trimethylamine triborane-7 have been carried out. Interesting results were obtained but do not bear on the present problem and are discussed in a separate section below.

Sodium triborohydride was obtained by reaction of diborane with sodium amalgam in diethyl ether.[17] In some cases the reaction product containing both sodium boronhydride

and sodium triborohydride was used for reactions. In others the triborohydride was separated by crystallization using diethyl ether.

In the initial reaction the crude mixture of borohydride and triborohydride was treated with hydrogen chloride in the initial absence of diborane. (Of course, reaction of HCl with $NaBH_4$ rapidly formed diborane in the system.) Vigorous reaction occurred at 0°C and was apparently complete after 15 minutes. Diethyl ether was used as a solvent for the reaction. Despite the absence of diborane in the initial mixture a 17% yield of tetraborane was formed together with much smaller quantities of higher hydrides, in addition to hydrogen. Presence of diethyl ether complicated separation of the products. In a second reaction, the triborohydride was extracted with diethyl ether, desolvated by pumping in vacuum and treated with a mixture of diborane and hydrogen chloride. No reaction occurred during one half hour at -80° nor in one half hour at -45°C. At 0°C generation of hydrogen was essentially completed within fifteen minutes, but the components were allowed to stand for an additional two and one-quarter hours to attempt to drive the reaction to completion. Under these conditions an 18.3% yield of tetraborane was formed but no traces of higher hydrides were observed. Data obtained in these and subsequent experiments are summarized in Table 3.

Discussion.- In all of the experiments carried out no yield of tetraborane above 20% was obtained. However, it is of considerable importance to observe that only in the case where no diborane was initially present were even trace amounts of hydrides higher than tetraborane produced. Since it is apparent that decomposition of the B_3H_9 intermediate to diborane by the reverse of reaction 7 must occur to considerable extent, formation of tetraborane in any yield is of considerable interest. It must be recognized that no proof has been presented that tetraborane arises from B_3H_7 formed in the system nor in fact that B_3H_7 may be prepared in this fashion. However, correspondence between reaction products observed and the mechanism postulated above offer some support for the presumption that the triborane intermediate in pyrolysis of diborane is converted first to tetraborane and subsequently to other reaction products.

Table 3

Reactions of NaB_3H_8 with Acids and Diborane

Exp.	Reactants					Solvent	Conditions		Products and Yields
	NaB_3H_8	$NaBH_3$	HCl	B_2H_6	BF_3		Temp.	Time	
1	4	4	-	10	20	10 ml. diethyl ether	-80°C -45°C 0°C	2 hr. 2 hr. 2 hr.	No reaction No reaction Mixture of H_2 and hydrides
2	3.92	3.92	11	--	--	5 ml. diethyl ether	0°C	15 min	B_4H_{10} .68 mmoles 17% yield. Higher hydrides 0.3 mmoles and H_2
3	1.05	--	1.26	4.35	--	none	-80°C -45°C 0°C	30 min 30 min 2.5 hr	No reaction No reaction B_4H_{10} 0.19 mmoles 18.3% yield. H_2 evolved.
4.	0.85	0.85	3.55	4.41	--	none	0°C	1 hr	B_4H_{10} 0.089 mmoles 10.5% yield. H_2 evolved
6	5.2	5.2	12.1	11.8	--	none	0°C	45min	B_4H_{10} 0.94 mmoles 18% yield. H_2 evolved
7	2.85	--	4.4	4.95	--	10 ml. n-butyl ether	0°C	45min	A reaction occurred but no gaseous product was obtained.
8	2.12	--	4.95	3.55	--	none	0°C	1 hr	No reaction was observed.

Purified from H_2O

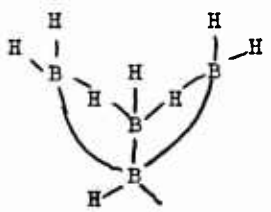
All numbers represent millimolar quantities unless stated otherwise.

It should be observed that the only product isolated in major yields from decomposition of diborane is pentaborane-11 and tetraborane-10 is present in only minor amounts. However, it must be recognized that tetraborane could not be a major product since under the reaction conditions it is known to be rapidly converted to pentaborane-11.[18,19] Furthermore, in the experiments of Klein and coworkers[20] in which diborane is decomposed in an apparatus consisting of a hot wall and a cold wall held close together (wherein initial reaction products would be expected to rapidly condense on the cold wall), one finds the overwhelming share of higher hydrides formed is, in fact, tetraborane. Inclusion of tetraborane as an intermediate in pyrolysis of diborane seems desirable.

Conversion of Tetraborane-10 to Pentaborane-11

The kinetics of conversion of tetraborane-10 to pentaborane-11 have been studied previously by Pearson and Edwards and by Dupont.[18,19] Both investigations showed that the conversion of tetraborane to pentaborane-11 was first order in tetraborane and independent of diborane concentration. Pearson and Edwards suggested that the elimination of borane in the rate controlling step produced the B_3H_7 molecule which subsequently reacted with diborane to produce pentaborane-11. This mechanism may be discarded, however, since diborane should exert an inhibiting influence on the reaction and such is not the case. Dupont on the other hand has suggested that the rate controlling step involves the elimination of the molecule of hydrogen from tetraborane-10 to form tetraborane-8 which subsequently reacts in a rapid step with diborane to produce pentaborane-11 and eliminate a borane molecule (to enter the facile diborane equilibrium). Such a mechanism is consistent with the observed kinetics of the reaction. It was deemed desirable to obtain direct information concerning the nature of the intermediate molecule formed in the initial decomposition of tetraborane-10. A classical method of obtaining such information is to divert the reactive intermediate to other products.

Some consideration should again be given to possible structures for the B_4H_8 molecule. Application of the topological theory of Lipscomb shows as possibilities 4020, a 3111, and a 2202 structure. Attempts to derive a satisfactory structure based on an icosahedral fragment are unsatisfactory. If other regular geometrical figures are considered, a satisfactory tetrahedral 4020 structure may be devised but within the limiting assumptions of Lipscomb's theory, no satisfactory structure may be found. On the other hand, if vacant orbital structures are considered utilizing the equations developed above, structures of the 1205, 2112, and 3021 types must be considered. Tetraborane-10 itself contains only 2 BH_2 groups and it appears unlikely that loss of hydrogen should produce more such groups. Moreover, consideration of possibilities based on an icosahedral fragment fails to yield a proper structure of a 1203 type. In similar fashion, a 3021 structure is not found to be satisfactory (indeed is impossible if the additional assumption of topological theory of the necessity of a mirror plane of symmetry is accepted). Two structures of the 2112 type can be drawn. However, in one case the vacant orbital is pointed toward the interior of the molecule and directly towards the electrons in the localized single bond. Such an arrangement appears totally unsatisfactory. The second structure shown below



appears to be a satisfactory structure within the limits of the topological framework and indeed appears to be the only satisfactory one which can be constructed for the B_4H_8 molecule.

The above considerations lead one to consider the probability that a tetraborane-8 molecule will be a reactive Lewis acid. In the presence of a Lewis base sufficiently weak so that interaction with the tetraborane-10 molecule does not occur, the stronger Lewis acid tetraborane-8 might form a stable adduct. Carbon monoxide

seems to provide an ideal choice for such a base. Furthermore, Burg has previously reported the formation of a tetraborane-8 carbonyl from tetraborane itself and carbonmonoxide,[20,21]

Experimental. To avoid subsequent decomposition of a product expected to be thermally unstable, the reaction of tetraborane and carbon monoxide was carried out in a flow system with recirculation of carbon monoxide but not of boranes. This was accomplished by circulating carbon monoxide with an all glass circulating pump first into a U-tube containing liquid B_4H_{10}, then into a reaction zone maintained at 120°C, thence directly into a liquid nitrogen trap. Under these conditions excellent conversion of tetraborane to B_4H_8CO was obtained.

In a typical reaction 10.11 mmoles of B_4H_{10} were condensed into a U-tube at -195°C and a large excess of carbon monoxide was added. The U-tube was then warmed at -45° and the gaseous mixture pumped through a U-tube maintained at 120°, into another U-tube cooled with nitrogen. Most of the tetraborane was held as a liquid in the -45° trap and only slowly transferred through the hot zone. When all of the tetraborane had left the -45° tube, the non-condensable gases were pumped from the system through cold traps and the condensable materials introduced into the fractionation apparatus. Tetraborane-10 was removed from the compound by fractionation through a -95° trap and was further purified by additional fractional condensations. In this experiment 7.15 mmoles of tetraborane-10 were recovered. For ultimate purification of the compound for physical studies, the impure tetraborane carbonyl was subjected to a number of quick fractionations through a -80° trap. When approximately half of the substance had passed into the colder trap, the more volatile fraction was again re-fractionated trapping the majority of the substance in a -95° trap. For the substance used for mass spectral determination the sample was again subjected to a final slow distillation through a -95° trap and a small portion passing into a trap maintained at -112° was utilized for the determination. The closeness of vapor pressures of tetraborane carbonyl and the pentaboranes made

the complete purification of this substance by conventional fractional distillation procedures a difficult if not impossible task.

Vapor tensions of the material observed at five temperatures are compared with those reported by Burg in Table 4. Table 5 records the major peaks of the infrared spectrum of the sample. Table 6 presents the major peaks of the polyisotopic mass spectrum of the sample obtained with the mass spectrometer described above. The nuclear magnetic resonance spectra of this material were obtained with the cooperation of Dr. Robert Williams of the Olin Mathieson Corporation Laboratory in Pasadena, California. These spectra are shown in Figure 3.

At 120°C no non-volatile or slightly volatile byproducts were formed in the reaction. Borane carbonyl and traces of higher boron hydrides were observed in small quantities and pentaboranes and diborane proved particularly difficult to free from the samples. The ^{11}B nuclear magnetic resonance spectrum does not appear to be grossly affected by the presence of other boranes as impurities. The high field doublet observed in this compound occurs at substantially higher field than the doublet in tetraborane itself or in other boron hydrides. The small peak falling between the apparent doublet and the apparent triplet probably arises from other borane contamination and does not appear to be of sufficient intensity to interfere substantially with the interpretation of the spectrum. The mass spectrum reported is corrected for the presence of a slight pentaborane-9 impurity. No correction could be made for the presence of diborane, however, owing to the peaks arising in this region from the carbonyl itself. The presence of diborane as a persistent impurity in this material is somewhat surprising and suggests that the mode of decomposition of the substance may continually produce diborane as an impurity. It is felt, however, that the mass spectrum of the substance above mass 28 is a close approximation to that of the pure compound.

Table 7 presents some data on the rate of disappearance of tetraborane under the experimental conditions employed. Rough rate calculations based upon the observed kinetics of conversion of tetraborane-10 to pentaborane-11 produce a rate

Table 4. Vapor Pressures of B_4H_8CO

t°	P_{mm} observed	P_{mm} literature[+]
-63.5	1.12	1.07
-49.5	3.24	3.61
-45	4.24	4.78
-30.5	11.48	12.65
0.0	69.40	71.3

[+]Burg

Table 5. Infrared Spectrum of B_4H_8CO

Wave length	Intensity	Remarks
3.85-4.05	Strong (sharp)	Split into two peaks
4.35	Weak (sharp)	
4.65-4.75	Strong	Medium sharp
5.2	Strong	Sharp
5.6	Very weak	
6.2	Weak	
6.3	Weak	
6.4	Weak	
6.5-6.7	Strong	Broad
7.0	Weak	
8.6-8.8	Strong	Broad
9.4-9.65	Strong	Broad
11.1-11.4	Strong	Broad
12.5	Medium	Broad

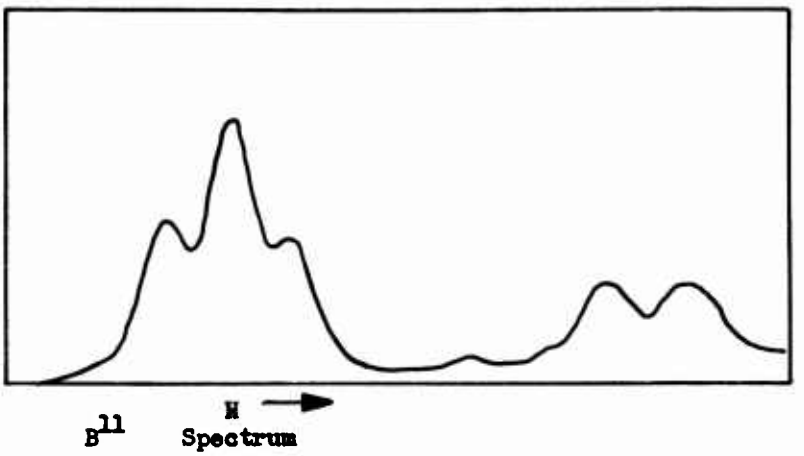
Table 6. Polyisotopic Mass Spectrum of B_4H_8CO

m/e	Intensity	m/e	Intensity
52	3.40	28	100
51	9.07	27	12.9
50	48.9	26	12.0
49	50.2	25	7.65
48	50.9	24	11.0
47	39.3	23	5.85
46	22.5	22	1.70
45	12.7	21	.34
44	7.94	14	3.22
43	4.30	13	15.7
42	1.14	12	10.3
41	.68	11	24.2
40	--	10	6.45
39	1.93	--	--
38	17.4	--	--
37	16.0	--	--
36	14.8	--	--
35	12.8	--	--
34	6.91	--	--
33	2.78	--	--
32	1.36	--	--
31	--	--	--
30	--	--	--
29	1.58	--	--

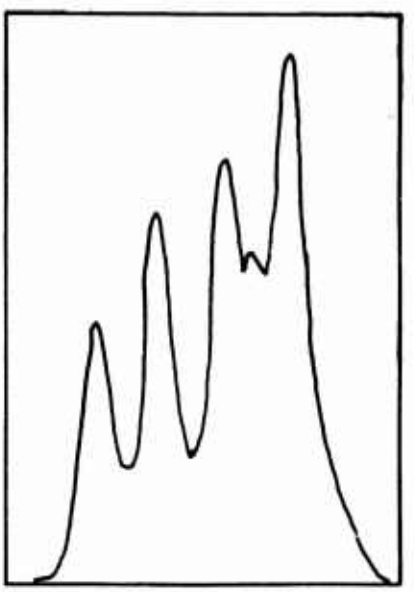
Sensitivity 14.4 div/μ for m/e = 48
compared to 238.3 div/μ for m/e = 41 for butene-1

Figure 3

NMR Spectra of B_4H_8CO



B^{11} H Spectrum



H^1 H Spectrum

Table 7. Rate of Formation of B_4H_8CO

Run	mmoles B_4H_{10} init.	mmoles B_4H_{10} final	Temp. °C	Time Min	B_4H_{10}/Time
1	10.11	7.15	120	61	.05
2	7.15	5.85	120	35	.04
3	5.85	4.27	120	28	.057
4	9.72	7.48	120	33	.068
5	7.48	6.74	100	62	.012
6	6.57	4.67	100	60	.032
7	10.94	9.25	100	77	.027

of disappearance of tetraborane within a factor of 2 of that observed in the present experiments suggesting a common rate limiting step. Further experiments will be carried out during the coming year on the kinetics of this reaction and to determine activation energy. It should be observed that at 130° and above non-volatile yellow products as well as a white sublimable solid is formed.

The compound B_4H_8CO is unstable at room temperature and undergoes decomposition to produce carbon monoxide and an as yet unidentified product. The purified material seems to have much higher stability than the crude reaction product containing borane carbonyl, tetraborane-10, and other hydrides in smaller quantites. It was consequently of interest to consider the reaction of B_4H_8CO with other compounds and two have thus far been studied briefly. On treatment with excess diborane at room temperature for eighteen minutes only a trace of carbon monoxide was produced in addition to a small amount of oily non-volatile material. No increase in the higher boron hydride content of the sample could be observed mass spectrometrically. In similar fashion, a mixture of tetraborane-10 and B_4H_8CO in a ratio of five to one was allowed to stand for fifteen minutes at 27°C. At the end of this time only a trace of non-condensable gas had been formed and tetraborane-10 was recovered quantitatively from the reaction mixture. It should be observed that the rate of decomposition of the carbonyl in these experiments was slower than that of the pure carbonyl.

In a brief preliminary experiment pentaborane-9 was treated with carbon monoxide at 120°C in the same apparatus used for the preparation of B_4H_8CO. The mass spectrum of pentaborane sample was unchanged after the reaction and no evidence for incorporation of carbon monoxide into the molecule was obtained.

Discussion.- Some comments on the physical properties of tetraborane carbonyl should be made. The mass spectrum presented in Table 6 bears a striking resemblance to that of tetraborane-10 itself. No parent ion was observed and in fact the mass spectrum is almost a complete duplicate of that of tetraborane-10 above mass 28. The peak at mass 28 stands out as clear evidence for the presence of

carbon monoxide in the molecule and is nearly twice the intensity of any other peak in the spectrum. Complete absence of the parent peak is by no means unknown in the mass spectrometry. Indeed, tetraborane-10 itself shows no $B_4H_{10}^+$ ion. It is tempting to speculate that electron bombardment of tetraborane-10 in the mass spectrometer produced a $B_4H_8^+$ ion identical to that formed by the carbonyl.

The infrared spectrum of the sample shows the absence of carbon-hydrogen or oxygen-hydrogen stretching frequencies but a characteristic carbonyl absorption at 5.2 microns. Apparently no substantial alteration of the carbonyl group has occurred. The doublet stretching frequency in the BH region of the spectrum indicates the presence of residual BH_2 groups in the molecule.

The nuclear magnetic resonance spectra of the compound may perhaps be best discussed with view to the B_4H_8 structure derived from topological theory above. If the carbonyl group has occupied the vacant orbital position on the central boron, the molecule still contains two equivalent BH_2 groups, two bridge protons and two non-equivalent BH groups. The ^{11}B resonance spectrum may be expected to contain a 1:2:1 absorption of intensity corresponding to 2 BH_2 groups in addition to 2 doublets, not necessarily overlapping, arising from the BH groups. Reference to the spectrum in figure 3 shows that the weak doublet at the high field side of the spectrum can arise from only a single BH group in the molecule. Presumably the second doublet falls under the BH_2 triplet giving rise to the observed asymmetry. The proton spectrum of the compound contains insufficient detail to be of use in confirming these observations. It should be specifically observed that the nuclear magnetic resonance data do not as yet uniquely establish the structure of the compound although they are in agreement with the postulated structure. Further work along this line is contemplated during the coming year.

SECTION III

STUDIES OF ISOTOPICALLY LABELLED DECABORANE

Introduction

The chemistry of decaborane has proved to be both interesting and varied. Relatively few detailed structural investigations of decaborane and related materials have been reported. Both X-ray determinations and nuclear magnetic resonance studies have been carried out but for structural studies the first method suffers from the time consuming nature of the determinations and the second from the paucity of information contained in the ordinary decaborane spectrum. It was felt that considerable information concerning the general position of attack of various reagents on the decaborane molecule could be obtained through the use of isotopically labelled substances. In some thorough and beautiful experiments Shapiro and co-workers[22] studied both the nature of the original product of exchange of decaborane with D_2O and the nature of the subsequent rearrangement products. In relatively gentle treatments substantially all deuterium introduced in this manner is retained near the top of the decaborane molecule (5, 6, 7, 8, 9 and 10 positions). Studies of the reaction with labelled decaborane with acetonitrile and with methyl Grignard reagent have been made and are reported below.

Reaction of Decaborane with Acetonitrile

Early in the course of the present work some efforts were made to follow the kinetics of the reaction of acetonitrile with decaborane. The extreme variability of the results obtained prompted us to turn to the isotopic studies detailed below. At the time of undertaking these studies the structure of the $B_{10}H_{12} \cdot 2\ CH_3CN$ was unknown. Recently Lipscomb has shown that the product contains a linear acetonitrile group substituted at the 6-9 positions of the molecule with two remaining hydrogen bridges.[22] This structure is in agreement with the observation that hydrogen replaced during the reaction of the bridge labelled decaborane contains substantial

quantities of deuterium. Furthermore, apparently one bridge and one non-bridge hydrogen are eliminated during the reaction implying rearrangement of the molecule during the course of the reaction to place one of the protons originally in a bridge position in a terminal position.

Experimental.- Isotope analyses were carried out with the Consolidated Engineering mass spectrometer described above. The mass spectrometer was adjusted to give optimum peaks with hydrogen-deuterium mixtures and was calibrated with known mixtures. Essentially linear calibration to 70% deuterium was obtained.

Deuterated decaborane samples were prepared by two methods. Samples 1, 2, and 3 in table 8 were prepared by dissolving decaborane to form a saturated solution in dioxane, adding deuterium oxide slowly until decaborane precipitated, which was then quickly filtered, dried and sublimed. Samples 4-8 were obtained by quenching the dioxane solution in liquid nitrogen. Water and dioxane were then sublimed without allowing the frozen solution to melt. Decaborane was subsequently purified by sublimation. A portion of sample 8 was fused before using to equilibrate bridge with the 6,9 terminal positions.

Isotopic analysis of partially deuterated decaborane was carried out by subliming about 10 mg. of the substance through a quartz tube containing steel wool heated to 1000°C. Deuterium content of the total hydrogen evolved was determined mass spectrometrically. In calibration runs the method was shown to release greater than 99.5% of the expected hydrogen. In most cases samples were checked with the infrared spectrophotometer to show absence of deuterium in the terminal position.

Reactions were carried out by placing a weighed portion of the decaborane in a 25 ml. bulb, condensing in pure acetonitrile and sealing from the vacuum system. Bulbs were heated for a desired period of time in a constant temperature bath and then quenched by immersing in liquid nitrogen. The bulbs were then opened, hydrogen recovered, and subjected to mass spectrometric analysis. The results of a number of determinations are shown in Table 9.

Table 8. Mass Spectral Analysis of Bridge Deuterated Decaborane

Sample No.	Peak Intensities m/e = 2	m/e = 3	m/e = 4	% D	% D in Bridge
I	1704	1425	190	27.1	94.8
II	996	700	110	25.4	89.9
III	7500	2058	156	121.8	42.6
IV	975	694	126	26.3	92.0
V	2640	810	66	13.35	46.8
VI	1920	1320	244.5	26.0	91.1
	1850	1300	208	25.9	90.7
					90.9 Average
VII	2250	1020	123	19.1	66.9
	2145	1068	143	20.1	70.4
					68.6 Average
VIII	2013	1292	217	24.9	87.0
	2065	1362	236	21.5	87.6
					87.3 Average

Table 9. Deuterium Content of Gas Released by Treatment of Bridge Deuterated Decaborane with Acetonitrile

Sample No.	% D in Bridge	% D in Gas Evolved	%D Expected [1]	mg $B_{10}(HD)_{14}$ / ml CH_3CN	Reaction Temperature	Reaction Time
I_A	94.8	44.3	47.9	5.28	81.0	3 hr.
I_B	94.8	36.2	47.9	5.81	R.T.	5 days
II_A	89.9	35.5	45.0	5.91	81.0	3 hr.
II_B	89.9	29.6	45.0	5.74	R.T.	5 days
II_C	89.9	31.7	45.0	5.85	81.0	(same sample gas removed every 15 min.)
II_D	89.9	31.8	45.0	5.85	81.0	
II_E	89.9	31.9	45.0	5.85	81.0	
III_A	42.6	15.4	21.3	5.60	81.0	(same sample gas removed every 15 min.)
III_B	42.6	14.3	21.3	5.60	81.0	
III_C	42.6	14.0	21.3	5.60	81.0	
III_D	42.6	13.6	21.3	5.60	81.0	
IV_A	92.0	15.4	46.0	5.58	60.0	15 min.
V_A	46.8	18.3	23.4	57.0	78.8	15 min.
VI_A	90.9	37.0	45.5	76.4	78.8	5 min.
VI_B	90.9	37.0	45.5	76.4	78.8	5 min.
VII_A	68.6	32.1	34.3	16.7	78.8	5 min.
VII_B	68.6	28.8	34.3	16.7	78.8	2 1/2 min.
VII_C	68.6	32.3	34.3	16.7	78.8	1 min.
VII_D	68.6	29.0	34.3	16.7	78.8	10 min.
$VIII_A$	87.3	31.1	43.7	20.6	78.8	5 min.
$VIII_A$*	87.3	31.2	43.7	20.1	78.8	5 min.

*$B_{10}(HD)_{14}$ fused before reaction

Discussion.- Examination of the data presented in Table 9 clearly indicates that some hydrogen originally present in bridge positions is eliminated as the acetonitrile molecules enter the decaborane structure. The percentage of deuterium in the evolved hydrogen is far too low to correspond to elimination of two bridge protons. In general, the percentage of deuterium is also below that expected for elimination of one bridge and one terminal position. However, the deuterium content of the evolved gas is far higher than would be expected for random elimination of hydrogen. The most likely interpretation of these experiments appears to be that the hydrogen molecule eliminated contains one bridge and one non-bridge proton. Several explanations may be given for the low deuterium values observed. Slow drift of deuterium from bridge to 6,9 positions during the course of the reaction would be expected to lead to low deuterium content in the evolved hydrogen provided a 6,9 proton is not also eliminated during the reaction. Indeed, the percent deuterium observed in the evolved gas frequently approaches closely to that expected for an equilibrium distribution between bridge and 6,9 positions and never falls below the value for such a distribution. Although samples I and II show substantially less deuterium content in the evolved gas after longer time intervals, a more systematic study of this effect in samples IIC-IIE and IIIA-IIID failed to provide supporting evidence over shorter time intervals. It should be also observed that in no experiments were 100% bridge deuterated materials utilized. It would be entirely reasonable to expect an isotope effect on the kinetics of the reaction in the direction of more ready elimination of the protons remaining in bridge positions and leading to abnormally low deuterium content of the evolved gas.

It is at present our belief that the hydrogen evolved when acetonitrile reacts with decaborane arises by elimination of one bridge proton and one proton from the 5, 7, 8, 10 positions. Mechanisms can readily be devised explaining such elimination but discussion of these should await further experimental studies.

Reaction of Decaborane with Methyl Magnesium Iodide

Siegel and coworkers have demonstrated that decaborane reacts readily with methyl Grignard reagent to form a decaborane Grignard.[24] These authors have demonstrated that either a mono- or a di-Grignard reagent can be prepared suggesting that one of the two-fold positions in the decaborane molecule may be involved. Reaction of decaborane mono-Grignard reagent with benzyl chloride leads to the formation of a benzyl decaborane. Examination of the NMR spectrum of this substance showed only that substitution had not occurred at the 2-position. It has been suggested by these workers that substitution occurs in the molecule in a position asymmetrical with respect to the boron atom in the 2-position. These factors suggest that substitution occurs on the 6,9 position at the top of the decaborane molecule. Reaction could occur at either the bridge or terminal position with rearrangement of the resulting Grignard reagent to a terminal position. Alternatively, such rearrangement might occur during reaction with benzyl chloride; in any event it is unlikely that the benzyl remains in a bridge position.

It was considered possible to test the general area of attack on the molecule by examining the isotopic composition of the methane eliminated when bridge deuterated decaborane is treated with methyl magnesium iodide.

Experimental.- Samples of the previously described bridge deuterated decaborane were used for these studies. To minimize the possibility of ether-catalyzed re-arrangement of deuterium atoms from bridge to terminal positions, reactions were carried out by adding etheral solutions of methyl magnesium iodide directly to solid decaborane. Reaction occurred rapidly and gases evolved during the first ten seconds were collected in the vacuum system. Methane was separated from less volatile materials by passage through -196° C trap and examined mass spectrometrically. The data obtained are shown in Table 10. Reference spectra of CH_3D and CH_4 are given in Table 11.

Discussion.- It is apparent from examination of the data presented in Table 10 that substantial amounts of mono-deutero methane are produced in the reaction. Deuterium content of the methane collected is, however, much lower than expected

Table 10. Analysis of Methane Produced by Reaction of Bridge Deuterated Decaborane with Methyl Grignard Reagent

$B_{10}(HD)_{14}$ Sample No.	Mass Spectra of Methane Evolved Relative Peak Height					% CH_3D
	m/e = 14	m/e = 15	m/e = 16	m/e = 17	m/e = 18	
I	11	72	100	30	0.9	24.6
II	18	74	100	26	1.1	25.8
VIII*	18	80	100	13.7	0.9	13.3

*$B_{10}(HD)_{14}$ fused before reaction.

Table 11. Mass Spectra of Methane and Monodeuteromethane

	m/e = 14	m/e = 15	m/e = 16	m/e = 17	m/e = 18
Pure CH_3D	6	20	80	100	1.0
Pure CH_4	14.8	88.8	100	1.81	0

for attack at the bridge position. Two simple explanations are possible for the low values observed. Despite precautions to avoid drift of deuterium from bridge to terminal positions, such rearrangement may have occurred with the resulting low deuterium values. Alternatively, a substantial kinetic isotope effect in the displacement might be expected.

In any event, data presented are in better agreement with attack at the 5-10 positions of the molecule. Substitution at the 1,3 or 2,4 positions seems now highly unlikely. If one accepts formation of a di-Grignard reagent as indicative of substitution in a two-fold position, only the 6,9 positions remain.

SECTION IV

REACTIONS OF TRIMETHYLAMINE TRIBORANE-7

During the course of the investigations described in Section II of this report, some study was made of the reaction of trimethyl amine triborane with hydrogen chloride in the presence of diborane. Reactions proved complex but interesting and investigation of the substances produced is still underway.

A new and convenient synthesis of the desired B_3H_7 complex has been developed.

Preparation of the desired borane complex was carried out by reacting NaB_3H_8 with trimethylamine hydrochloride in diethyl ether solution. After reaction at room temperature for three hours, solvent was removed and the temperature of the flask raised until additional hydrogen was evolved (80-100°C). When hydrogen evolution was complete, the flask was opened and the contents sublimed to effect purification. Crude yields of about 50 percent were obtained in this manner. It is probable that higher yields could be attained if larger quantities of starting materials were utilized. The amine complex was further purified by recrystallization from methanol and resublimation.

In a typical reaction somewhat less than 4 mmoles of trimethylamine triborane was allowed to react with excess hydrogen chloride and diborane. A total of 3.29 mmoles of hydrogen was evolved during the course of the reaction and 3.23 mmoles of the gaseous diborane-hydrogen chloride mixture were absorbed. Analysis of the recovered mixture of gases was carried out by hydrolysis with methanol, titration of the hydrogen chloride was a strong acid followed by titration of the boron in the presence of the mannitol. The reaction was found to have consumed 1.06 mmole of diborane and 2.17 mmoles of hydrogen chloride. The solid products of reaction could all be sublimed from the reaction flask and no trimethylamine hydrochloride was formed.

Analysis of the sublimed material is as yet incomplete. Examination of the x-ray diffraction of the substance showed it to be a disordered solid and prevented estimation of its molecular weight. The solid density, however, is about 0.99. The crystals are formed as transparent plates which are rapidly covered by an opaque film on standing in air. The substance in its present state of purity exhibits a melting point between 75 and 100°C. Attempts to estimate its molecular weight by freezing point lowering of benzene gave a variable result between 100 and 150 (perhaps owing to the rapid attack of the substance in air).

Microanalysis of the compound for nitrogen and chlorine shows 12.9 and 19.6% respectively. These results do not, however, appear trustworthy. Analysis in our laboratory for chlorine in the hydrolyzed substance gave 26% from which it may be calculated that the minimum molecular weight of the material is 137.

Crude stoichiometry observed for this reaction indicates the possibility that an amine derivative of a substituted tetraborane has been formed (the indicated formula is at present $(CH_3)_3NB_4H_9Cl$). Additional study of this interesting material will be carried out during the coming year.

Treatment of trimethylamine triborane with hydrogen chloride in the absence of diborane also produces hydrogen and a sublimable product. The infrared spectrum of this material suggests that it is different from the product obtained in the presence of diborane, but the compound did not react with diborane subsequently added. This compound also will receive further attention during the coming year.

SECTION V

PREPARATION OF A NEW SOLID BORON HYDRIDE

Several years ago in the course of investigation of the decomposition of diborane in a silent discharge, we acquired considerable stocks of tetraborane. At that time no use of the material was contemplated and it constituted something of a hazard to store. It was consequently decided to convert it to more useful materials by decomposing for one-half hour at 100° to obtain decaborane. At a considerably later date the bulbs were opened, the volatile materials removed, and the contents extracted with carbon disulfide. Examination of the residue showed that in addition to the usual yellow solids, there were present a few single crystals looking like decaborane but insoluble in the common solvents for that substance. Examination of several crystals by x-ray diffraction showed that they were remarkably similar to decaborane in many ways. Thus, the space group of the new substance was the same as the disordered unit $B_{10}H_{14}$ and the lattice contents were 7.88, 10.73, and 6.03, compared to 7.225, 10.44 and 5.68. On a Fisher-Johns apparatus the substance melted over a considerable range, 230-250°. The minimum density of a single crystal was determined by a flotation method found to be 1.76 gs per cc. Assuming four molecules per unit cell, the minimum molecular weight is thus 135.1. The properties of the material are more in line with those expected for a substance of a higher molecular weight, perhaps a polymer, and it may well be that the assumption of four molecules per unit cell was incorrect. In any event, a unit containing 12 boron atoms was suggested by the data.

Further analysis of the data proved difficult. Examination of the Patterson projections of two zones showed no great structure at expected interatomic distances. Rather, large peaks were distributed in almost perfect six fold symmetry around the origin suggesting hexagonal packing of balls (quite in line with the proposal of polymeric structure based on a 12 boron fragment).

No further work had been carried out on this problem during the succeeding years and it appeared of interest to attempt to prepare additional quantities of the material.

Preparation of solid boron hydrides other than decaborane has not been undescribed in the literature. By pyrolysis of tetraborane-10, Stock obtained non-volatile materials of at least two types; one of these was a non-crystalline yellow material soluble in carbon disulfide whereas the other was a crystalline white soluble solid.[25] (In addition a non-crystalline yellow soluble substance appeared to be present also.)

Experimental.- Several exploratory experiments have been carried out during the past year but as yet the desired substance has not been isolated. Consequently, these will be only briefly described although considerable effort has been devoted to this phase of the investigation.

In a typical experiment a sample of tetraborane was condensed into a flask, sealed from the vacuum system and immersed for thirty minutes in a steam bath (this procedure closely duplicates that wherein the unknown crystalline solid was produced). Both yellow and white solids were formed during the reaction and settled to the lower portion of the flask. In addition to the usual volatile materials which were removed in the vacuum system, the flask contained decaborane in a very small amount of white, non-volatile material. Non-volatile yellow solids partially soluble in carbon disulfide were, of course, also produced. A large fraction of the decaborane was removed by sublimation and the residual yellow solids extensively extracted with carbon disulfide. Examination of the yellow solids under polarizing microscope showed them to be mostly yellow, powdery and of a non-crystalline nature. A few extremely small crystals appeared to be present but no single crystal was successfully mounted for x-ray investigation. The amount of white solid adhering to the flask walls was too small to be conveniently treated and did not appear to contain sizable crystals.

In other investigations mixtures of gaseous boron hydrides of various compositions have been treated. In most cases small samples of crystalline material carbon disulfide insoluble and non-volatile (and thus probably not decaborane) were formed. In no case have we been able to isolate sufficient material for either analysis or x-ray investigation.

The reaction of diborane with molten decaborane proved particularly interesting. About six mmoles each of diborane and decaborane were heated together for 38 minutes at 100°C in a horizontally positioned rotating glass cylinder. Yellow solids formed mainly on the area of the cylinder which had been covered by molten decaborane during the heating. Following removal of the major fraction of the decaborane by distillation and several washings of the residual non-volatile material with carbon disulfide, several successive carbon disulfide extractions of the yellow solids were carried out. Pumping of the carbon disulfide extract produced a viscous material which after chilling briefly with liquid nitrogen produced a multitude of small crystals. An attempt to determine the infrared spectrum of the material was unsuccessful owing to the rapid evolution of a gas. Such instability is not characteristic of decaborane solutions.

In a repetition of this experiment, additional quantities of the crystalline material were obtained. In no case did it prove possible to mount a single crystal of the substance for examination.

The tedious and difficult nature of the experiments reported above cannot be over-emphasized. However, the tantalizing prospect of isolating a new solid boron hydride, even in extremely small yield, prompts us to spend additional effort in this area. Studies of these and other systems will be continued throughout the coming year.

References

1. Stock, A. and Masseniz, C., Ber., 45, 3529 (1912).
2. Schlesinger, H. I. and Burg, A.B., J. Am. Chem. Soc. 53, 4321 (1931).
3. Schlesinger, H. I. and Brown, H. C., Ibid. 62, 3429 (1940).
4. Schlesinger, H. I. et al, Ibid., 75, 186-224 (1953).
5. Boone, J. L. and Burg, A. B., Ibid., 80, 1519 (1958).
6. Boone, J. L. and Burg, A. B., Ibid. 81, 1766 (1959).
7. Bragg, J. K., et al, Ibid. 73, 2134 (1951).
8. Clarke, R. P. and Pease, R. N., Ibid. 73, 2132 (1951).
9. Dickerson, A. R. and Lipscomb, W. H., J. Chem. Phys., 27, 212 (1957).
10. Hough, W. V. and Edwards, L. J., J. Am. Chem. Soc., 78, 689 (1956).
11. Brown, H. C. and Johannesen, R. B., Ibid., 75, 16 (1953).
12. Brown, H. C. and Kanner, B., Ibid., 75, 3865 (1953).
13. Lipscomb, W. N., Advances in Inorganic Chemistry and Radiochemistry, Vol. I, p. 133. Academic Press, New York, New York.
14. Clinton, W. L. and Rice, B., J. Chem. Phys., 30, 542 (1959).
15. Schlesinger, H. I. and Brown, H. C., J. Am. Chem. Soc., 62, 3429 (1940).
16. Sanderson, R. T., Vacuum Manipulation of Volatile Compounds. New York, John Wiley and Sons, Inc., 1948.
17. Hough, W. V. and Edwards, L. J., J. Am. Chem. Soc., 78, 689 (1956).
18. Pearson, R. K. and Edwards, L. J. Abstracts of Papers presented at the 132nd Amer. Chem. Soc. Meeting in New York, 1957, p. 15N.
19. Dupont, J., M.S. Thesis, Iowa State College, 1958.
20. Burg, A. B. and Spielman, J. R., ONR Contract Nonr-228(13) Task No. NR052050 TR4.
21. Burg, A. B. and Spielman, J. R., J. Am. Chem. Soc. 81, 3478 (1959).
22. Shapiro, I., Lustig, M. and Williams, R., Abstracts of papers presented at the 134th Meeting of the American Chem. Soc. in Chicago, September, 1958, p. 25N.
23. Reddy, J. and Lipscomb, W. N., J. Am. Chem. Soc. 81, 754 (1959).
24. Siegel, B. et al, Ibid., 80, 4523 (1958).
25. Stock, A., Friederici, K. and Priess, Ber., 46, 3353 (1913).